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TiO_2 coatings obtained by reactive sputtering at room temperature: Physical properties as a function of the sputtering pressure and film thickness

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ABSTRACT

TiO_2 layers with crystalline anatase structure have been attained on unheated glass substrates, by reactive sputtering from a metallic target, using the sputtering pressure to change the energy of the particles arriving to the film surface. Such energy and the time of plasma exposure also influence the morphology and other physical properties of the sputtered films. The deposition time has been ranged to obtain TiO_2 coatings with different thicknesses from 0.24 to 1.08 μm and at various total pressures from 0.2 to 1.0 Pa. Overall characterization of the samples has been performed by X-ray diffraction, atomic force microscopy and spectrophotometry. The effects of the sputtering pressure and the film thickness on the crystalline structure (interplanar distance and mean crystallite size), the morphology (roughness and surface area) as well as the optical properties (refractive index, extinction coefficient) have been established. A direct relation between optical and morphological characteristics, and the calculated film porosity has been proven. Such porosity is well controlled by the deposition parameters; these allow tuning the optical and morphological properties of the sputtered TiO_2 coatings as required for different applications.

1. Introduction

Over the last decades, the TiO_2 semiconductor has attracted a great interest owing to its low-cost and low-toxicity together with its high transparency, high refractive index, and good chemical stability. Nowadays, TiO_2 thin films are used for a variety of applications, ranging from selective absorbing coatings to photovoltaic solar cells, gas sensors and photocatalysis [1–4]. The two main crystalline phases of TiO_2 (anatase and rutile) have been obtained in thin film form. Rutile is preferred for protective coatings on lenses or elevated temperature operations owing to its higher refractive index and thermal stability [5], whereas the anatase phase has shown a better photocatalytic performance due to longer electron-hole lifetimes [6]. The combination of rutile and anatase has also revealed a good photocatalytic activity, enhancing the optical absorption and the separation of photogenerated charges for adequate interfaces [7,8]. Furthermore, TiO_2 thin films have the ability of tuning their morphological properties according to the particular application. Densely-packed smooth coatings are good blocking layers in solar cell applications [2,9,10], whereas porous coatings offer higher active surfaces that are preferred for gas sensors and photocatalysis [4,11]. Apart from the crystalline structure and surface roughness, the TiO_2 film behavior depends on its band gap energy and optical absorption coefficient, being the specific values highly dependent on the layer thickness and other deposition conditions [11–13].

The preparation of TiO_2 thin films by sputtering has prominent advantages such as clean process (without intermediate chemical products), high reproducibility and easy scale-up to produce uniform films on large area substrates. Different sputtering processes have been used for TiO_2 deposition, in radio frequency (RF) or direct current (DC) modes, from pure metal [14–17] or metal oxide [2,11–13] targets. In general, reactive DC sputtering from conductive (Ti or TiO_{2-x}) targets is preferred for large-scale production due to its high deposition rate and ease of process control [7,14]. The highest rates (above 15 nm/min) are achieved by setting the deposition conditions in the metal-oxide transition region (that is at low oxygen partial pressures), which gives TiO_2 thin films with rutile phase or amorphous [14–16], whereas crystallization of the anatase phase requires additional annealing at 350 °C or above [12,14,17]. Pure anatase TiO_2 has been only obtained by sputtering in oxide conditions, and its growth is highly dependent on the working gas pressure [18,19]. This is because the energy of the particles arriving to the film surface should be adjusted to reach the threshold needed for anatase formation but not exceed it to avoid a disordered atomic distribution (amorphous) or the rutile phase activation [17,18]. The sputtering gas pressure can be used for such energy regulation since it influences the probability of collisions

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and the acceleration of particles, but it also modifies the growth rate and the surface morphology in different ways [19–21]. Samples with different thickness are often compared and more investigations are needed to evaluate separately the influence of the gas pressure and the layer thickness on the physical properties of anatase thin films.

In the present work, anatase TiO_2 thin films have been obtained on unheated glass substrates by reactive DC sputtering from a Ti target, minimizing the thermal cost of the preparation process. The oxygen partial pressure was fixed, near to the metal-oxide transition to maintain a high deposition rate, whereas the total (argon + oxygen) pressure and the deposition time have been varied in a wide range. Effects of the sputtering pressure and the film thickness on the crystalline structure, morphology and optical properties of the TiO_2 coatings have been determined. The main objective has been to explore variations in the anatase growth that allow the establishment of consistent correlations between the deposition parameters (sputtering pressure and film thickness) and the layer porosity, which in fact determines the surface roughness and the optical absorption coefficient.

2. Experimental details

Titanium oxide coatings have been prepared at room temperature on soda-lime glass substrates (SLG, 2 mm thick) by reactive DC magnetron sputtering of a Ti (99.6% purity) metallic target with 176.7 cm^2 area. The sputtering source was operated at a constant power density of 8 W/cm^2, which is low enough to produce no substantial substrate heating. The deposition chamber was first evacuated to a base pressure of $2 * 10^{-4}$ Pa, and then raised to an upper value in the 0.20–1.00 Pa range by the introduction of reactive (O_2) and working (Ar) gases through separated mass-flow controllers. The partial pressures $P(O_2)$ and P(Ar) were increased proportionally, maintaining constant the oxygen ratio $X(O_2) = P(O_2)/[P(O_2) + P(Ar)] = 0.20$. In a previous work, the Ar partial pressure was fixed at 0.08 Pa and the O_2 partial pressure was varied in the 0.02–0.04 Pa interval, giving rutile TiO_2 films at the lowest oxygen proportion ($X(O_2) = 0.20$) and amorphous layers at higher oxygen ratios [22]. Here, the gases magnitudes have been changed in order to achieve anatase TiO_2 formation and to study the effect of the total sputtering pressure. Besides, the deposition time has been varied to obtain different layer thickness in the 0.24–1.08 μm range and to analyze the influence of this other parameter on the anatase TiO_2 properties.

The film thickness was determined by post-deposition measurements with a Dektak 3030 profilometer. The crystallographic structure of the samples was examined by X-ray diffraction (XRD) using Cu Kα1 ($\lambda = 1.54056$ Å) radiation in a Philips X'pert instrument with Bragg-Brentano θ–2θ configuration, on a same illuminated area of 1×1 cm^2. The crystalline phases have been analyzed by comparison of the measured diffraction peaks with the cards given by the Joint Committee of Powder Diffraction Standards (JCPDS). The mean crystallite size has been estimated with the Scherrer formula from the full width at half-maximum of the main diffraction peak. The morphology was characterized with a Park XE-100 atomic force microscope (AFM) in the non-contact mode, by taking digital images that allow quantification of the roughness and the surface area. The optical properties were determined from transmittance and reflectance measurements in the 300–1500 nm wavelength range with a Perkin-Elmer Lambda 9 spectrophotometer.

3. Results and discussion

Firstly, the effect of the total pressure on the deposition rate was established. The target voltage and the film growth rate are found decreasing when the pressure is increased, as stated by the experimental data shown in Fig. 1. The same behavior has been observed for other sputtering processes performed at a fixed power [17,19], although different variations are also reported [20,21] because an increase in the sputter current may result in a rise of the sputtering yield and the deposition rate [23]. In the present conditions, the increment in the working pressure decreases the mean free path and the energy of the ionized gas species, and then the sputtering yield of target diminishes. Concurrently, the energy of the sputtered metallic particles decreases according to the diminution of the target self-bias with respect to the grounded substrate.

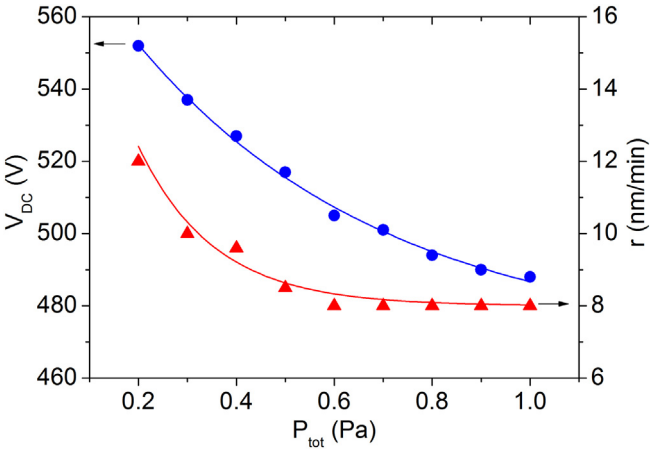

Fig. 1. Evolution of the target self-bias and the film growth rate as a function of the total sputtering pressure.

The influence of the total pressure on the crystalline structure of the samples is illustrated in Fig. 2, which includes the XRD patterns of TiO_2 layers grown with a same thickness of 0.48 μm at different pressures from 0.2 to 1.0 Pa. Such equal thickness was obtained by adjusting the deposition time according to the growth rate depicted in Fig. 1 for the various pressures. All films exhibit the anatase phase, identified by the main (101) peak located around $2\theta = 25.3°$ and other minor peaks (JCPDS card no 21–1272). These other anatase peaks, specially (004) and (220) reflections, become more important when the sputtering pressure increases above 0.6 Pa. Otherwise, for the layer prepared at the lowest pressure of 0.2 Pa, the presence of rutile has been detected by the (110) peak located at $2\theta = 27.4°$ (JCPDS card no 21–1276). The coexistence of anatase and rutile crystalline phases is a common feature of sputtered TiO_2 thin films [13], being a general tendency that the rutile peak intensity increases with the process power [24] while the height of the anatase peak rises with the increment in the oxygen partial pressure [16,25], which decreases the discharge voltage [23]. Here, the evolution from mixed phases to pure anatase layers has been achieved by

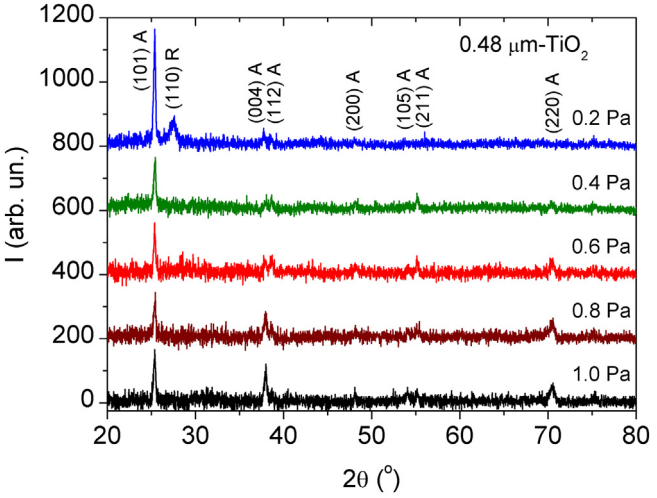

Fig. 2. Diffractograms corresponding to TiO_2 films with 0.48 μm thickness obtained at sputtering pressures ranging from 0.2 to 1.0 Pa. Peaks are assigned to the anatase (A) and rutile (R) phases.